Photoluminescent two-dimensional coordination polymers constructed with octanuclear silver(I) clusters or silver(I) ions

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Two silver(I) coordination polymers have been synthesised and single-crystal structural analysis shows that 1 is the first coordination network containing discrete silver clusters and organic *N*,*N*′-spacers. It displays an intense blue photoluminescence with three emission maxima.

The design of coordination polymers is an area of intense current interest. In particular, as many functional materials in the fields of catalysis, separation, absorption, and molecular recognition, optics and electromagnetism manifest themselves as two- or three-dimensional networks, it is important to be able to generate various high-dimensionality systems with both novel structural topologies and functional properties.[1–3] While most of these reported inorganic-organic hybrid materials are constructed by mononuclear metal centres with polydentate ligands, less attention has been paid to the use of metal clusters as building units for the synthesis of new multidimensional structures.[3d,4] Metal clusters may exhibit versatile coordination capacities, rigidity and intriguing physical properties, the coordination polymers constructed with metal clusters as building blocks are usually very stable and hence more promising in potential applications than those assembled with mononuclear metal centres. However, the synthesis of hybrid materials composed of metal cluster building blocks is still a great challenge. We present here two novel two-dimensional coordination networks consisting of 2,2′-bis(2-pyridyl)ethene (2,2′-bpe) bridges and unprecedented $Ag_8(SO_4)_4$ clusters or Ag(I) ions, namely $[Ag_8(\mu_4\text{-}SO_4)_4(2,2'\text{-bpe})_5]\cdot 10H_2O$ (**1**) and $[Ag_2(2,2'\text{-bpe})_3(NO_2)_2]$ (**2**), which exhibit blue emissions at ambient and cryogenic temperatures.

Reactions between 2,2′-bpe and silver(I) salts in a 1:1 molar ratio in MeCN–H_2O gave compounds $[Ag_8(\mu_4\text{-}SO_4)_4(2,2'\text{-bpe})_5]\cdot 10H_2O$ (**1**) and $[Ag_2(2,2'\text{-bpe})_3(NO_2)_2]$ (**2**). The elemental analysis confirmed the formula of **1** and **2**. It is interesting to note that complex **1** is the unique product when the molar ratio of Ag(I) and 2,2′-bpe was changed to 1:2 in the reaction system, suggesting that the reaction is insensitive to the stoichiometry.

X-Ray crystallography has established that **1** consists of a two-dimensional coordination network comprising unusual $Ag_8(SO_4)_4$ clusters and 2,2′-bpe bridges. For each $Ag_8(SO_4)_4$ cluster, the four SO_4^{2-} groups display the same μ_4 bridging mode to connect eight Ag(I) atoms into an unprecedented octanuclear cluster possessing crystallographic inversion symmetry, as shown in Fig. 1. It should be noted that such a binding mode of the sulfate ion is different from those observed in related complexes.[5] The Ag(2) atom is coordinated in a distorted tetrahedral geometry by three sulfate μ-oxygen atoms and one 2,2′-bpe nitrogen atom, while each of the Ag(1), Ag(3) and Ag(4) atoms is coordinated in a Y-shaped geometry by two sulfate oxygen atoms and one 2,2′-bpe nitrogen atom [for Ag(1) and Ag(3)] or by one sulfate oxygen atom and two 2,2′-bpe nitrogen atoms [for Ag(4)]. It should be noted that the Ag(1)···Ag(2) and Ag(2)···Ag(3a) distances are 3.236(1) and 3.237(1) Å, respectively, which are longer than the metallic Ag–Ag contact (2.89 Å), suggesting very weak Ag···Ag interactions.[6]

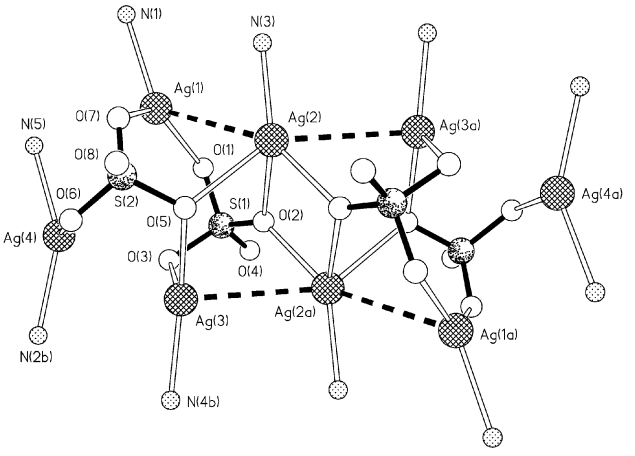

Fig. 1 Perspective view of the $Ag_8(SO_4)_4$ cluster in **1**.

The distinguishing feature of **1** is that adjacent clusters are covalently linked by non-coplanar 2,2′-bpe bridges [dihedral angles 22.6(3) and 6.8(2)°] and coplanar 2,2′-bpe bridges, resulting in an interesting two-dimensional coordination slab, as shown in Fig. 2. To the best of our knowledge, coordination networks constructed from discrete silver clusters and organic spacers are very rare, only a related three-dimensional network with Ag_4 clusters and succinate anions has been documented; in this case the succinates act both as bridges and for charge compensation.[7] Therefore, **1** represents the first coordination network containing discrete silver clusters and organic *N*,*N*′-spacers.

The crystal structure of **2** consists of a neutral two-dimensional network. Each Ag(1) atom is ligated by three nitrogen atoms from two non-coplanar and one coplanar 2,2′-bpe ligands, and further ligated by a chelating nitrite group, completing an irregular five-fold coordination at Ag(I) . The non-coplanar 2,2′-bpe ligands [dihedral angle 22.1(3)°] bridge the Ag(I) atoms into helical chains. Adjacent chains are racemic and are further linked by the coplanar 2,2′-bpe ligands into an interesting two-dimensional network of (6,3) topology (Fig. 3). The framework of **2** is, to our knowledge, the third known two-dimensional herringbone architecture, the other

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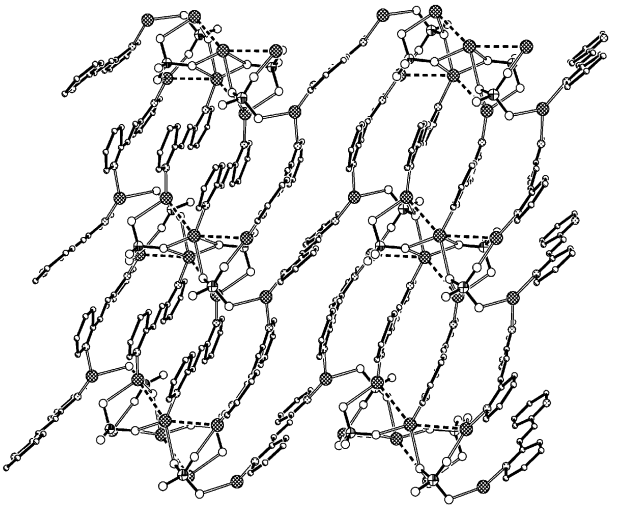

Fig. 2 Perspective view of the two-dimensional network in **1**.

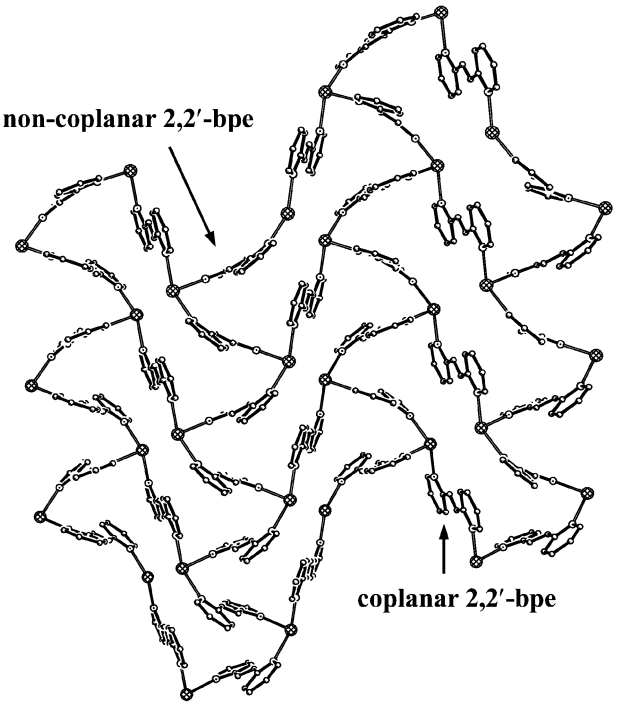

Fig. 3 Perspective view of the two-dimensional network in **2**. The nitrite anions are omitted for clarity.

two examples being found in two coordination polymers with octahedral metal centres.[8]

Ag(I) polymers are markedly more sensitive to ligand and anion functionality and to solvent systems compared to other transition metal polymers.[1c] Thus, within a related series of complexes, all grown under similar conditions, comparison can lead to a greater understanding of the individual contributions of ligand and anion functionality. The most notable effect of the change in anion was found in the case of Ag(I) complexes with 1,4-bis(4-pyridyl)-2,3,4,5-tetrazine.[1c,9] In our case, the effect of anion functionality is illustrated by the complexes presented here. Replacement of the weakly coordinating BF_4^- anion[10] by more strongly coordinating NO_2^- and SO_4^{2-} anions has a profound effect upon network geometry, the structure motifs vary from a one-dimensional chain, to a (6,3) net, to a two-dimensional slab. It should also be noted that the product formed is the same regardless of the reaction

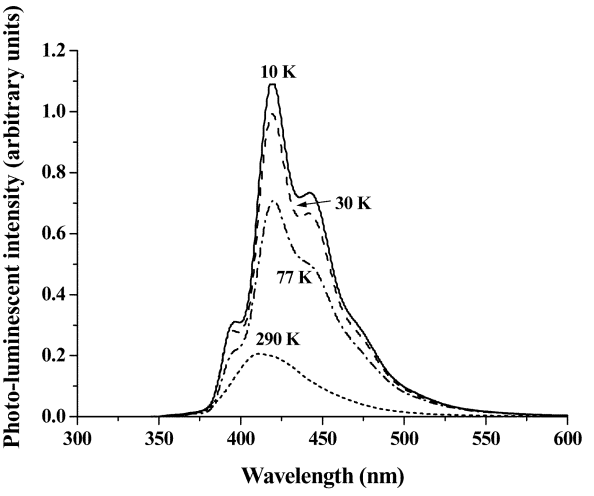

Fig. 4 Solid state photo-induced emission spectra of **1** at ambient and cryogenic temperatures with $\lambda_{ex} = 325$ nm.

stoichimetery for **1**, suggesting that the bridging SO_4^{2-} anions play a vital role in the construction of the network of **1**.

Commonly, most luminescent Ag(I) compounds exhibit emission at low temperature. Some important examples are organometallic silver(I) compounds[11a] using acetylides as the bridging ligands, silver(I)-diisocyanide[11b] and silver(I)-cyano[11c] compounds. Only a few monomeric and polymeric Ag(I) complexes emit luminescence at room temperature,[3a,b,e,12] However, in our case, crystals of both **1** and **2** are luminescent at both ambient and cryogenic temperatures. More interestingly, upon excitation at 325 nm **1** displays intense blue photoluminescence with three emission maxima at 398, 420 and 443 nm, which are quite well-resolved at low temperature (Fig. 4), whereas **2** displays intense blue photoluminescence with only one emission maximum at 422 nm upon excitation at 325 nm. It has been suggested that the emissions in the reported silver(I) complexes originate either from $d\sigma^*$-$p\sigma$ transitions, or from 4d-5s transitions, or from excited states of a metal-to-ligand charge transfer (MLCT) or having MMLCT character.[13] In this work, the emissions may be related to the different coordination geometries. There are three types of coordination polyhedrons ($AgNO_2$, AgN_2O and $AgNO_3$) in **1**, but only one in **2**.

In summary, we present two novel photo-luminescent two-dimensional coordination polymers constructed with octanuclear silver(I) clusters or silver(I) ions. The isolation of **1** and **2** demonstrates that the anion plays an important role in the self-assembly process of these architectures.

Experimental

An MeCN solution (10 cm^3) of 2,2′-bpe (1.0 mmol) was added dropwise to a stirred MeCN–H_2O (1:1 v/v) solution (5 cm^3) of Ag_2SO_4 (0.5 mmol) or $AgNO_2$ (1.0 mmol) at 50 °C over 15 min. After several days at room temperature, colourless plate crystals precipitated (yield 75% and 90% for **1** and **2**, respectively). Anal. calcd for $C_{60}H_{70}Ag_8N_{10}O_{26}S_4$ (**1**): C, 30.82; H, 3.02; N, 5.99%. Found: C, 30.76; H, 2.94; N, 5.90%. Anal. calcd for $C_{18}H_{15}AgN_4O_2$ (**2**): C, 50.61; H, 3.54; N, 13.11%. Found: C, 50.40; H, 3.45; N, 12.92%.

X-Ray crystallography

Data collections ($2° \leqslant \theta \leqslant 27°$ for **1** and **2**) were performed at 293 K on a Siemens R3m diffractometers (Mo-Kα, $\lambda = 0.71073$ Å). The structures were solved with direct methods and refined with full-matrix least-squares techniques

(SHELXL-97),[14] giving a final R_1 value of 0.0467 for 487 parameters and 5122 unique reflections with $I \geqslant 2\sigma(I)$ and wR_2 of 0.1196 for all 7355 reflections for **1**, a final R_1 value of 0.0504 for 227 parameters and 2130 unique reflections with $I \geqslant 2\sigma(I)$ and wR_2 of 0.1239 for all 3583 reflections for **2**. The relatively high sigmas on the crystallographical axes and the relative high thermal parameters in **1** and **2** mainly resulted from using an old diffractometer. CCDC reference numbers 163960 and 163961. See http://www.rsc.org/suppdata/nj/b2/b202481k/ for crystallographic data in CIF or other electronic format.

Crystal data for 1. $C_{60}H_{70}Ag_8N_{10}O_{26}S_4$, $M_r = 2338.45$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.554(7)$, $b = 12.210(8)$, $c = 14.290(5)$ Å, $\alpha = 82.97(1)^\circ$, $\beta = 80.82(1)^\circ$, $\gamma = 89.79(1)^\circ$, $U = 1804.0(18)$ Å^3, $Z = 1$, $\mu = 23.27$ cm^{-1}.

Crystal data for 2. $C_{18}H_{15}AgN_4O_2$, $M_r = 427.21$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.461(7)$, $b = 17.530(7)$, $c = 9.266(5)$ Å, $\beta = 108.20(1)^\circ$, $U = 1768.5(16)$ Å^3, $Z = 4$, $\mu = 11.58$ cm^{-1}.

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References

1 (*a*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*b*) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 575; (*c*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*d*) M. J. Zaworotko *Chem. Commun.*, 2001, 1; (*e*) M. Fujita *Chem. Soc. Rev.*, 1998, **27**, 417.

2 (*a*) Y.-H. Kiang, G. B. Gardner, S. Lee, Z.-T. Xu and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1999, **121**, 8204; (*b*) S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2081; (*c*) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158; (*d*) P. C. M. Duncan, D. M. L. Goodgame, S. Menzer and D. J. Willams, *Chem. Commun.*, 1996, 2127; (*e*) L. Carlucci, G. Ciani, M. Moret, D. M. Proserpio and S. Rizzato, *Angew. Chem., Int. Ed.*, 2000, **39**, 1506.

3 (*a*) M.-L. Tong, X.-M. Chen, B.-H. Ye and L.-N. Ji, *Angew. Chem., Int. Ed.*, 1999, **38**, 2237; (*b*) M.-L. Tong, X.-L. Yu and X.-M. Chen, *Inorg. Chem. Commun.*, 2000, **3**, 694; (*c*) M.-L. Tong, S.-L. Zheng and X.-M. Chen, *Chem. Eur. J.*, 2000, **6**, 3729; (*d*) J. Tao, M.-L. Tong, J.-X. Shi and X.-M. Chen, *Chem. Commun.*, 2000, 2043; (*e*) S.-L. Zheng, M.-L. Tong, S.-D. Tan, Y. Wang, J.-X. Shi, Y.-X. Tong, H. K. Lee and X.-M. Chen, *Organometallics*, 2001, **20**, 5319.

4 (*a*) H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (*b*) L. G. Beauvais, M. P. Shores and J. R. Long, *J. Am. Chem. Soc.*, 2000, **122**, 2763.

5 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 6th edn., 1999, p. 492.

6 (*a*) A. Bondi *J. Phys. Chem.*, 1964, **68**, 441; (*b*) M. Jansen *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1098; (*c*) P. Pyykkö *Chem. Rev.*, 1997, **97**, 597.

7 A. Michaelides, V. Kiritsis, S. Skoulika and A. Aubry, *Angew Chem., Int. Ed. Engl.*, 1993, **32**, 1495.

8 (*a*) Y.-B. Dong, R. C. Layland, N. G. Pschirer, M. D. Smith, U. H. F. Bunz and H. C. zur Loye, *Chem. Mater.*, 1999, **11**, 1413; (*b*) M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey and M. Schröder, *New J. Chem.*, 1999, **23**, 573.

9 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2327.

10 M.-L. Tong and X.-M. Chen, unpublished work.

11 (*a*) V. W. W. Yam, K. K.-W. Lo, W. K.-M. Fung and C.-R. Wang, *Coord. Chem. Rev.*, 1998, **171**, 17; (*b*) P. D. Harvey and D. Fortin, *Coord. Chem. Rev.*, 1998, **171**, 351; (*c*) M. A. Omary and H. H. Patterson, *J. Am. Chem. Soc.*, 1998, **120**, 7696.

12 (*a*) V. W. W. Yam, K. K.-W. Lo, C. R. Wang and K. K. Cheung, *Inorg. Chem.*, 1996, **35**, 5116; (*b*) V. J. Catalano, H. M. Kar and J. Garnas, *Angew. Chem., Int. Ed.*, 1999, **38**, 1979; (*c*) A. Vogler and H. Hunkely, *Chem. Phys. Lett.*, 1989, **158**, 74; (*d*) D. Fortin, M. Drouin, M. Turcotte and P. D. Harvey, *J. Am. Chem. Soc.*, 1997, **119**, 531; (*e*) B.-L. Fei, W.-Y. Sun, T. Okamura, W.-X. Tang and N. Ueyama, *New J. Chem.*, 2001, **25**, 210; (*f*) J. Fan, W.-Y. Sun, T. Okamura, J. Xie, W.-X. Tang and N. Ueyama, *New J. Chem.*, 2002, **26**, 199.

13 (*a*) C.-M. Che, M.-C. Tse, M. C. W. Chan, K.-K. Cheung, D. L. Phillips and K.-H. Leung, *J. Am. Soc. Chem.*, 2000, **122**, 2464; (*b*) P. C. Ford and A. Vogler, *Acc. Chem. Res.*, 1993, **26**, 220; (*c*) M. Henary and J. I. Zink, *Inorg. Chem.*, 1991, **30**, 3111; (*d*) A. Vogler and H. Hunkely, *Chem. Phys. Lett.*, 1988, **150**, 135.

14 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Analysis, University of Göttingen, Germany, 1997.